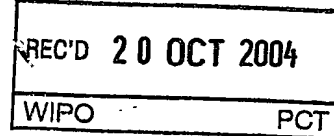




Europäisches  
Patentamt

European  
Patent Office

Office européen  
des brevets



Bescheinigung

Certificate

Attestation

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.

The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

03256030.2

**PRIORITY  
DOCUMENT**  
SUBMITTED OR TRANSMITTED IN  
COMPLIANCE WITH RULE 17.1 (a) OR (b)

Der Präsident des Europäischen Patentamts;  
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets  
p.o.

R C van Dijk

BEST AVAILABLE COPY



Anmeldung Nr:  
Application no.: 03256030.2  
Demande no:

Anmeldetag:  
Date of filing: 25.09.03  
Date de dépôt:

Anmelder/Applicant(s)/Demandeur(s):

SHELL INTERNATIONALE RESEARCH  
MAATSCHAPPIJ B.V.  
Carel van Bylandtlaan 30  
2596 HR Den Haag  
PAYS-BAS

Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:  
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.  
If no title is shown please refer to the description.  
Si aucun titre n'est indiqué se référer à la description.)

Solid oxide fuel cell-based auxiliary power unit

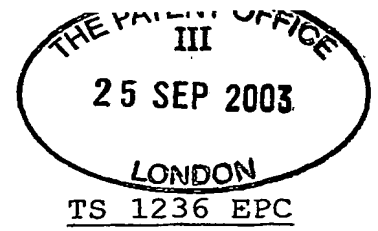
In Anspruch genommene Priorität(en) / Priority(ies) claimed /Priorité(s)  
revendiquée(s)  
Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation/International Patent Classification/  
Classification internationale des brevets:

H01M8/00

Am Anmeldetag benannte Vertragsstaaten/Contracting states designated at date of  
filing/Etats contractants désignées lors du dépôt:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LU MC NL  
PT RO SE SI SK TR LI



Haz

# SOLID OXIDE FUEL CELL-BASED AUXILIARY POWER UNIT

The present invention relates to an auxiliary power unit (APU) for electricity generation in combination with an internal combustion engine and to a process for the generation of electricity using such APU.

5       Solid oxide fuel cell (SOFC) technology has been developed for application in transportation industry, primarily as an on-board auxiliary power unit (APU). Among others, the SOFC-based APU technology provides electric power for passenger cars, for instance for airco  
10       systems, lightning, electric operating windows, break and steering systems, and the like.

      SOFC-based APU systems can make use of a reformer system for fuelling the system once started. The reformer of choice up to now is a partial oxidation reformer  
15       (CPOx) that uses fuel and air, and catalytically converts it to primarily hydrogen, carbon monoxide, and nitrogen. It is housed inside the hot box and operates at high temperature. Such reformers are, for instance, disclosed in WO 99/13521 and US 2002/0025458. The reformers  
20       according to the prior art are fed fuel and air through valves located in the main plenum chamber. The fuel is introduced through the insulated wall by way of an injector. The output from the CPOx mainly consisting of a carbon monoxide and hydrogen mixture is fed to the SOFC  
25       stack directly. This system has a few disadvantages, particularly the necessity to use heat exchangers, pre-heaters, and air blowers. These elements make the fuel system complicated and expensive. Further, according to WO 99/13521 and US 2002/0025458 the CPOx mixes

hydrocarboneous fuel with heated air to combust or oxidize the mixture. Such reformer allows a single fuel delivery to the SOFC, but develop very high temperatures in the reformer, leading to accelerated catalyst degradation and coke deposition.

For that reason there is a need for a method for using such units, which is devoid of these disadvantages.

It has now been found that these problems can be solved when the exhaust gas of an internal combustion engine is used to replace at least part of the oxygen. To this end the invention relates to an auxiliary power unit (APU) for electricity generation in combination with an internal combustion engine, the APU comprising

- 1) a solid oxide fuel cell (SOFC) comprising an inlet for fuel, an inlet for air and/or engine exhaust gas, and an outlet for off-gas, and
- 2) a catalytic partial oxidation reformer (CPOx) having an outlet which is connected to the inlet for fuel of the SOFC and an inlet for reactants, characterized in that the inlet for reactants is connected with the internal combustion engine through an evaporator having inlets for the reactants and an outlet which is connected to the inlet of the CPOx.

The advantages of this invention are inter alia that no heat exchangers are required because the heat is already available in the engine exhaust gas, whereas the overpressure of the engine exhaust gas makes the use of blowers, which lead to electric loss, redundant. The present method has more advantages over the prior art, for instance water is already present in the engine exhaust gas, making water recycling and evaporation superfluous. Further high adiabatic temperatures are avoided, less coke formation and thermal shock occur in

the SOFC leading to increased catalytic lifetimes, and moreover, start-up of the unit is simple when the engine exhaust gas has pre-heated the CPOx and SOFC to start-up temperature, whereas fuel consumption is held at a minimum.

The CPOx reactor into which the fuel, engine exhaust gas, and optionally an oxygen-containing gas (the feed) are routed includes a reactor or exterior wall, which may be of a cylindrical shape. The exterior wall may be constructed of metal, quartz or other materials, which can withstand temperatures up to about 1300° C and are substantially chemically inert to hydrocarbon oxidation or carbon formation. Suitable materials can include quartz-lined steel, high temperature ceramics, ceramic metal composites, nickel based superalloys, cobalt based superalloys, and in general, high temperature metals and metals protected by ceramic coatings. Within the exterior wall radiation shields to contain heat within a catalytic reaction zone, as well as to allow the feed to pass through the reactor, may be present. The shields may be configured in the shape of cylindrical plugs and made of a high temperature ceramic with an appreciable void volume (i.e., porosity). The shields can be made of materials such as zirconia, alumina, and cermets. The shields may be upstream and downstream of the reactor, but may also usefully be placed so as to surround or encase the reactor.

The shields define the area of a catalytic reaction zone where the partial oxidation reaction occurs. Further provided by the shields is a means for maintaining a catalytic reaction temperature within the catalytic reaction zone. Unless the reaction zone is at a particular reaction temperature, the partial oxidation

reaction cannot be initiated. Therefore, the reaction temperature within the reaction zone may initially be provided by hot engine exhaust gas.

5        However, a particular reaction temperature may have deleterious effects on CPOx processing, such as sulfur formation on the catalyst, incomplete oxidation, and by-product formation. To achieve the desired effects of the reaction temperature while seeking to avoid the deleterious effects, the reaction temperature is usefully  
10        maintained in the present invention at a range from about 600° C to 1200° C.

      Within the reaction zone is disposed the catalyst which serves to catalyze the step or act of partially oxidizing the feed. Although the catalyst can vary, the  
15        preferred embodiment of the present invention contemplates that the catalyst comprises a noble metal supported on a porous ceramic or metal monolith, preferably a ceramic foam. Preferred ceramic materials comprise zirconia. Thereby, the feed enters the reaction  
20        zone where it is contacted with the catalyst, with the contact being controlled by regulating the catalytic contact time. In large part, the contact time is controlled by the feed flow rate and configuration of the catalyst.

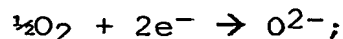
25        It is beneficial to maintain a liquid hourly space volume (LHSV) of greater than about 0.5 h<sup>-1</sup>, and preferably in the range of about 0.5 h<sup>-1</sup> to 75 h<sup>-1</sup>. LHSV is defined as the liquid hydrocarbon flow rate per unit volume of catalyst, with the catalyst volume defined  
30        as the volume occupied by the monolith. A more tortuous flow path created by the catalyst increases the contact time. The duration of the contact time is controlled in order to maximize partial oxidation and minimize further

oxidation of hydrogen and carbon monoxide. A useful contact time is not more than about 500 milliseconds. A preferred range of contact time is from about 10 to 500 milliseconds. More preferably, the contact time is about 50 to 200 milliseconds and, in particular, about 100 milliseconds.

As a result of the reaction parameters described above, the partial oxidation in the reaction zone produces synthesis gas that can exit the CPOx reactor. The synthesis gas substantially comprises hydrogen gas, carbon monoxide, carbon dioxide, water vapor, hydrogen sulfide, methane, traces of unconverted hydrocarbons, traces of other sulfur compounds, and nitrogen, if the oxidizer gas is engine exhaust gas, air or oxygen-enriched air.

The hot synthesis gas is discharged into the solid oxide fuel cell, in which optionally also another part of engine exhaust gas can be introduced. The SOFC is a fuel cell which is known in the art and which comprises a plurality of elements, each element comprising an anode layer and a cathode layer, separated from each other by means of a solid electrolyte layer. Charge transfer through the solid electrolyte layer from the cathode to the anode is done by oxygen ions.

The overall cathode reaction of a solid oxide fuel cell is:



and the overall anode reaction is:



The anode off-gas thus comprises carbon dioxide and water.

The elements of SOFC systems are known to the skilled person and are, for instance, either flat plates or tubes

to form a planar or tubular solid oxide fuel cell,  
respectively. A commonly used anode material comprises Ni  
and yttria-stabilised zirconia. The cathode layer is a  
porous layer of an electron-conductive ceramic material,  
5 typically a mixed metal oxide having a perovskite  
structure. Lanthanum-strontium-manganese oxides are a  
commonly used cathode material. The solid electrolyte  
layer of a solid oxide fuel cell is oxygen-ion conductive  
and has very limited conductivity for electrons. This  
10 layer is dense and impermeable to gases. Yttria-  
stabilised zirconia is commonly used.

In fuel cells, all elements, i.e. the tubes or  
plates, are electrically connected to each other.

During normal operation of the APU according to the  
15 invention, a hydrocarbonaceous fuel is fed via the inlet  
for fuel to the anode side of the elements. Preferred  
hydrocarbonaceous fuels comprise diesel, gasoline and  
special fuel cell grade fuel. In a preferred embodiment  
an oxygen-containing gas, preferably additional air, is  
20 pre-mixed with the engine exhaust gas and fed via the  
inlet for exhaust/air to the cathode side of each  
element. The cathode and anode reactions take place  
resulting in the generation of electricity and the  
production of anode off-gas comprising hydrogen, carbon  
25 oxides, water, and fuel at the anode side of the  
elements. Depleted air is formed at the cathode side of  
the elements.

Accordingly, the invention further relates to a  
process for the generation of electricity from a hydro-  
carbonaceous fuel, wherein in an auxiliary power unit as  
30 previously described:

a) both hydrocarbonaceous fuel and engine exhaust gas are  
introduced into an evaporator;



b) after which the evaporated or partly evaporated mixture of fuel and engine exhaust gas is introduced into a CPOx and converted into synthesis gas; and  
c) the synthesis gas is introduced into a SOFC to generate electricity.

5 In a preferred process the synthesis gas is introduced into the SOFC via the inlet for fuel and engine exhaust gas is introduced into the SOFC via the inlet for air and/or exhaust gas. In another preferred  
10 embodiment of the invention, engine exhaust gas is introduced into the evaporator as a mixture with an oxygen-containing gas, such as air.

The APU and the process according to the invention will be illustrated by means of the following Figure.

15 Fig. 1 shows a block diagram of an auxiliary power unit (APU) for electricity generation in combination with an internal combustion engine comprising a solid oxide fuel cell 9 comprising an conduit 6 for fuel, a conduit for air and/or engine exhaust gas 7, a conduit for  
20 off-gas 10, a catalytic partial oxidation reformer 5 having an outlet 6a which is connected via conduit 6 to the inlet 6b of the SOFC 9 and an inlet 4b for reactants. The reactants comprise hydrocarbonaceous fuel and as  
25 oxygen source at least engine exhaust gas, which are transported to the inlet of the CPOx 5 through an evaporator 3 having inlets 1,2 for the reactants (particularly, diesel, gasoline or special fuel cell grade fuel and exhaust gas) and an outlet 4a which is connected via conduit 4 to the inlet 4a of the CPOx 5.

25 SEP 2003

LONDON

TS 1236 EPC

C L A I M S

1. An auxiliary power unit (APU) for electricity generation in combination with an internal combustion engine, the APU comprising
  - 5 1) a solid oxide fuel cell (SOFC) comprising an inlet for fuel, an inlet for air and/or engine exhaust gas, and an outlet for off-gas, and
  - 2) a catalytic partial oxidation reformer (CPOx) having an outlet which is connected to the inlet for fuel of the SOFC and an inlet for reactants, characterized in that
    - 10 the inlet for reactants is connected with the internal combustion engine through an evaporator having inlets for the reactants and an outlet which is connected to the inlet of the CPOx.
2. A process for the generation of electricity from a hydrocarbonaceous fuel, wherein, in the auxiliary power unit of claim 1:
  - 15 a) both hydrocarbonaceous fuel and engine exhaust gas are introduced into the evaporator;
  - b) after which the evaporated or partly evaporated mixture of fuel and engine exhaust gas is introduced into the CPOx and converted into synthesis gas; and
  - 20 c) the synthesis gas is introduced into the SOFC via the inlet for fuel to generate electricity.
3. The process according to claim 2, wherein engine exhaust gas is introduced into the SOFC via the inlet for air and/or engine exhaust gas.
- 25 4. The process according to claim 2 or 3 wherein the engine exhaust gas is introduced into the evaporator as a mixture with an oxygen-containing gas.

5. The process according to claim 4, wherein the oxygen-containing gas is air.

6. The process according to any one of claims 2-5 wherein diesel or gasoline is used as the  
5 hydrocarbonaceous fuel, preferably diesel.



A B S T R A C T

SOLID OXIDE FUEL CELL-BASED AUXILLIARY POER UNIT

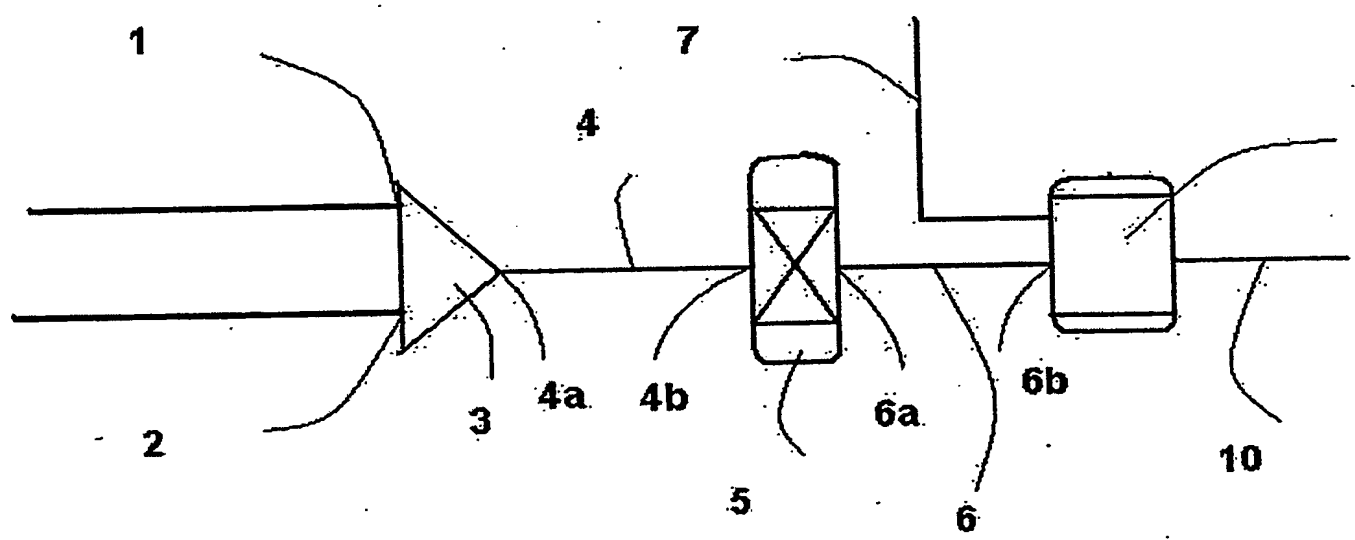
The invention relates to an auxiliary power unit (APU) for electricity generation in combination with an internal combustion engine, the APU comprising 1) a solid oxide fuel cell (SOFC) comprising an inlet for fuel, an inlet for air and/or engine exhaust gas, and an outlet for off-gas, and 2) a catalytic partial oxidation reformer (CPOx) having an outlet which is connected to the inlet for fuel of the SOFC and an inlet for reactants, characterized in that the inlet for reactants is connected with the internal combustion engine through an evaporator having inlets for the reactants and an outlet which is connected to the inlet of the CPOx. The invention further relates to a process for the generation of electricity from a hydrocarbonaceous fuel using such an APU.

(Figure 1)

TS 1256

THE PATENT OFFICE  
III  
25 SEP 2003  
LONDON

Fig. 1



**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

☒ **BLACK BORDERS**

☒ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**

☒ **FADED TEXT OR DRAWING**

☒ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**

☐ **SKEWED/SLANTED IMAGES**

☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**

☐ **GRAY SCALE DOCUMENTS**

☒ **LINES OR MARKS ON ORIGINAL DOCUMENT**

☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**

☐ **OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**